

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 April 2003 (17.04.2003)

PCT

(10) International Publication Number
WO 03/031520 A1

(51) International Patent Classification⁷: **C09B 62/20**

(21) International Application Number: PCT/IB02/04100

(22) International Filing Date: 7 October 2002 (07.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2001 1854/01 8 October 2001 (08.10.2001) CH

(71) Applicant (for all designated States except US): **CLARIANT INTERNATIONAL LTD** [CH/CH]; Rothausstrasse 61, CH-4132 Muttenz (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **GISLER, Markus** [CH/CH]; F.J. Dietschy-Weg 2, CH-4310 Rheinfelden (CH).

(74) Agent: **BIELEFELDT, Florian**; Clariant International Ltd, Rothausstrasse 61, CH-4132 Muttenz 1 (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

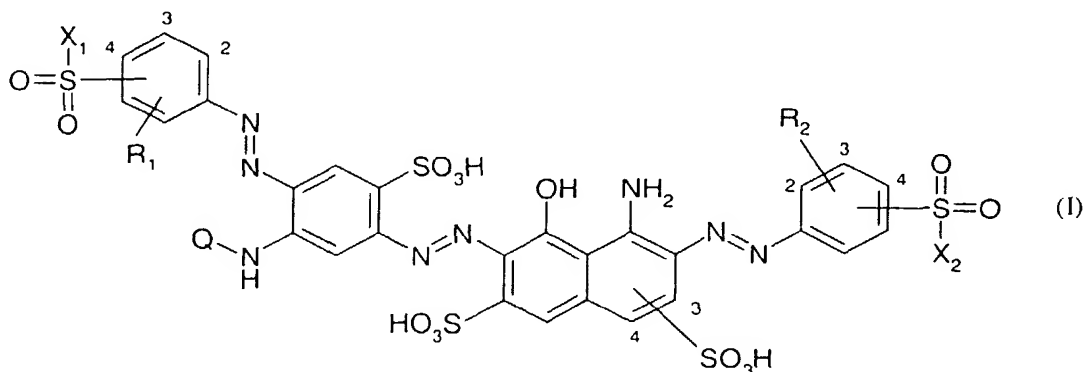
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ORGANIC COMPOUNDS



(57) Abstract: Fibre-reactive trisazo compounds of the formula (I) bearing halogenated pyrimidine reactive moieties and where the substituents are each as defined in the claims, and also the associated synthesis, the use of the compounds for dyeing or printing hydroxyl-containing or nitrogenous organic substrates, the use of the compounds as a component in an inkjet printing ink and also the dyed or printed substrates.



WO 03/031520 A1

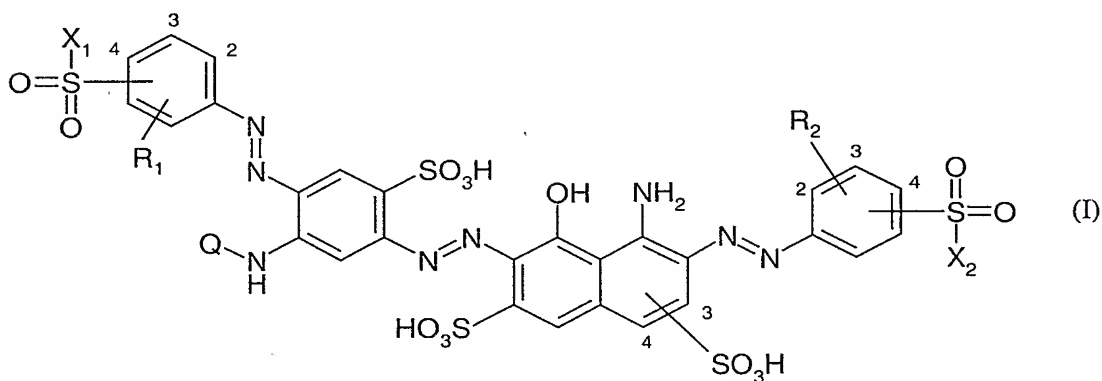
ORGANIC COMPOUNDS

This invention relates to novel fibre-reactive trisazo compounds bearing halogenated pyrimidine reactive moieties, and also to the associated synthesis, the use of the compounds for dyeing or printing hydroxyl-containing or nitrogenous organic substrates, the use of the compounds as a component in an inkjet printing ink and also the dyed or printed substrates.

Although reactive radicals of this type have already been disclosed in DE1644204 (US 3, 669,951), DE2114158 (US 4,065,446) and EP526792 (US 5,436,324), some of them still have problems in practical application.

Furthermore, reactive dyestuffs containing other reactive groups and various chromophores have already been disclosed in EP-A 45,278 and EP-A 65,479 and in German Offenlegungsschrift 2,817,780. These dyestuffs too still need to be improved.

This invention relates to novel fibre-reactive trisazo dyes of the formula (I)



where

X_1 and X_2 are independently $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}_2\text{Y}$, where Y is an alkali-detachable group,

R₁ and R₂ are independently H or -SO₃H, and

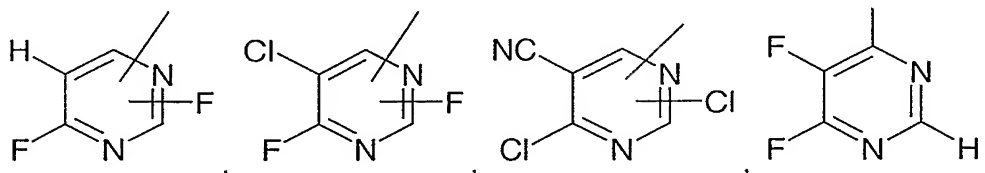
Q is a halogenated pyrimidine reactive radical,

and also their salts and mixtures thereof.

In preferred compounds of the formula (I),

X_1 and X_2 are each $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{Y}$, where each Y is independently $-\text{OSO}_3\text{H}$, $-\text{Cl}$ or $-\text{SSO}_3\text{H}$, and

5 Q is one of the following halogenated pyrimidine reactive radicals:

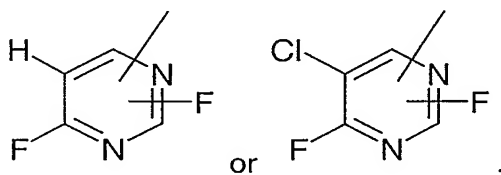


In particularly preferred compounds of the formula (I),

10

X_1 and X_2 are each $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$, and

Q represents the following pyrimidine reactive radicals:

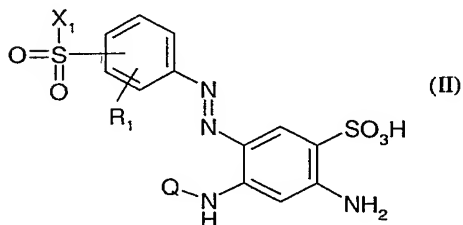


15

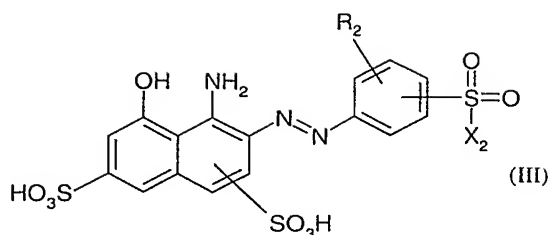
Useful salts include in particular alkali metal or alkaline earth metal salts.

A further aspect of this invention is the synthesis of the compounds of the formula (I)

20 whereby a compound of the formula (II)



is diazotized under the generally known conditions and coupled with a compound of
25 the formula (III)



under known conditions.

5 The compounds of the formula (I), their salts and mixtures thereof are reactive dyes. They are useful for dyeing or printing hydroxyl-containing or nitrogenous organic substrates and for use in inkjet printing inks for printing paper and optionally pretreated substrates.

10 Preferred substrates include leather and fibre materials comprising natural or synthetic polyamides or especially natural or regenerated cellulose, such as cotton, filament viscose or staple viscose.

The most preferred substrate is textile material comprising cotton.

15

The compounds of the formula (I) can be used in dyeing liquors or in print pastes by all dyeing or printing processes customary for reactive dyes. Preference is given to dyeing by the exhaust process, in which case a temperature interval of 30-80°C and preferably 50-60°C is employed.

20

The compounds according to the invention can be used as individual dyes or else, by virtue of their good compatibility, as a combination element with further reactive dyes of the same or other classes that have comparable dyeing properties, for example with regard to general fastnesses, exhaustion value, etc. The combination dyeings obtained

25 are just as fast as the dyeing with individual dye.

25

The compounds of the formula (I) attain good exhaustion and fixation values. The unfixed dye portion is readily washed off. The dyeings and prints obtained exhibit good wet fastness properties for example with regard to wash, water, seawater and perspiration fastness, and have good stability to oxidative influences such as to chlorinated water, hypochlorite bleach, peroxide bleach and also to perborate-containing laundry detergents.

30

This invention accordingly further provides a process for dyeing or printing hydroxyl-containing or nitrogenous organic substrates, wherein dyeing or printing is effected with the above-defined compounds, their salts or mixtures thereof.

5

The present invention yet further provides a hydroxyl-containing or nitrogenous organic substrate which has been dyed or printed as per the above-described dyeing or printing process.

10 The invention yet further provides substrates, especially cellulose, polyamides and animal fibres, preferably cotton, which have been dyed or printed with such compounds.

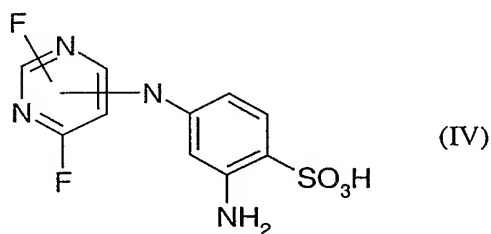
The invention similarly provides paper and optionally pretreated substrates comprising
15 cellulose, polyamides or animal fibres, printed with inkjet printing inks comprising such compounds, their salts or mixtures.

The examples which follow illustrate the invention. Parts are by weight and temperatures are reported in degrees Celsius, unless otherwise specified.

20

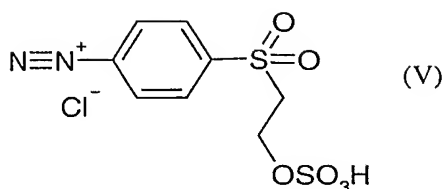
EXAMPLE 1

332 parts of a condensation product (formula (IV)) of 2,4-diaminobenzenesulphonic acid and 2,4,6-trifluoropyrimidine are prepared according to EP 526792.

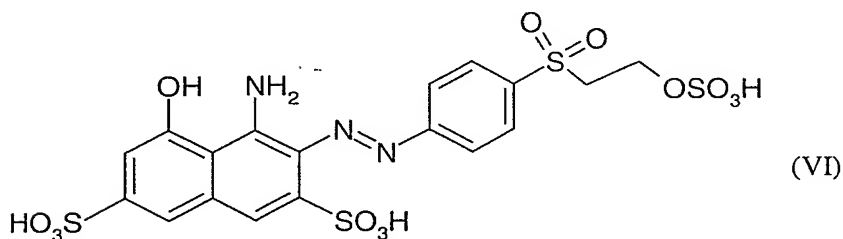


25

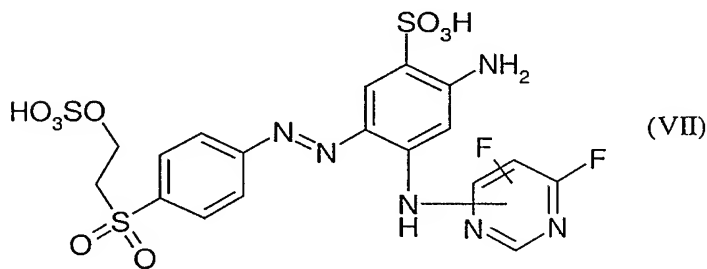
281 parts of 4-aminophenyl 2'-sulphatoethyl sulphone are suspended in a mixture of 600 parts of water and 300 parts of ice, admixed with 250 parts of 30% hydrochloric acid and diazotized at 0-5°C with 250 parts of 4N sodium nitrite solution. This affords
30 about 2 300 parts of a diazo suspension which contains 329 parts of the diazonium salt of the formula (V).



Meanwhile, 319 parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (H-acid) are suspended in 1 000 parts of water. The H-acid suspension is added to the
 5 diazonium suspension. The subsequent addition of about 750 parts of an approximately 15% sodium carbonate solution raises the pH to 5-6.



10 A further 281 parts of 4-aminophenyl 2'-sulphatoethyl sulphone are diazotized and added as the diazonium suspension to the reaction mixture of the formula (IV). The simultaneous metered addition of about 750 parts of an approximately 15% sodium carbonate solution maintains the pH at 3-4.

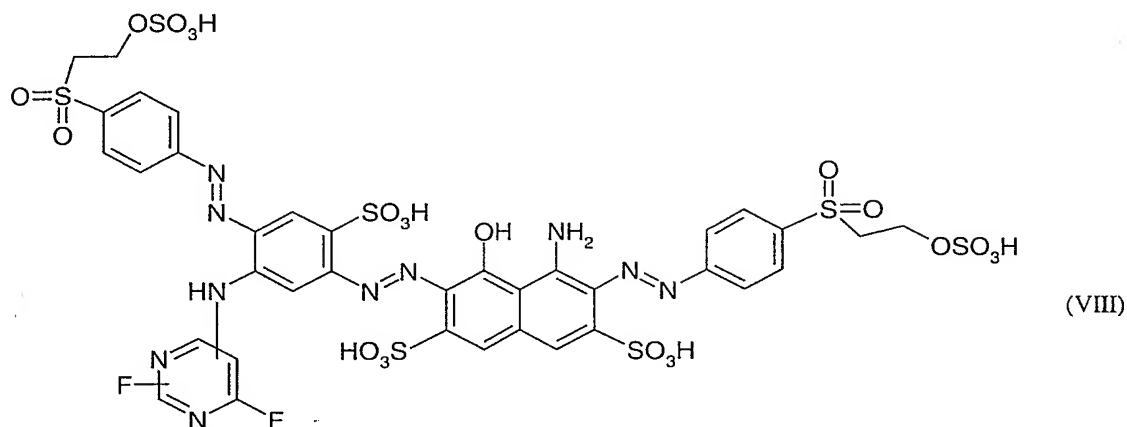


15

The resulting suspension of the monoazo dye of the formula (VII) is admixed with 240 parts of 30% hydrochloric acid, cooled to 0°C and diazotized with 240 parts of 4N sodium nitrite solution. The diazonium suspension thus prepared is added to the
 20 solution of the monoazo dye of the formula (VI). During the diazo addition, the pH of the reaction mixture is maintained between 7-7.5.

The solution is clarified and spray dried to obtain about 2 500 parts of a greenish black

salt-containing powder which dyes cellulose in deep bluish green shades. The dye conforms to the following formula (VIII):

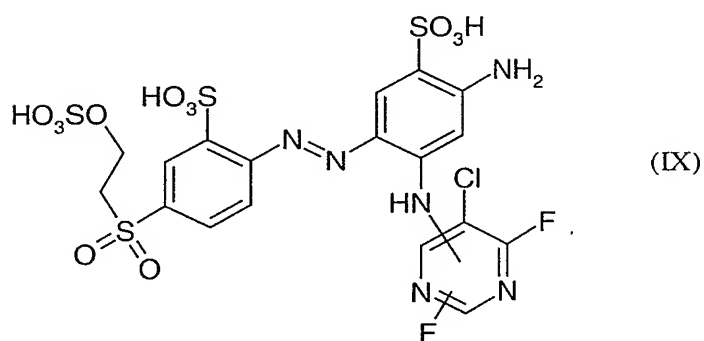


5

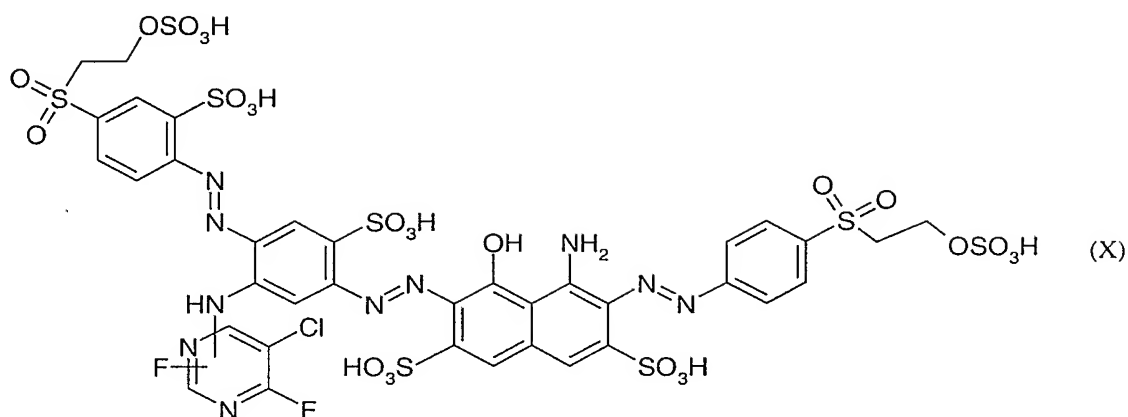
The dyeings possess excellent fastnesses and outstanding unfixed dye wash-off even in deep shades.

EXAMPLE 2

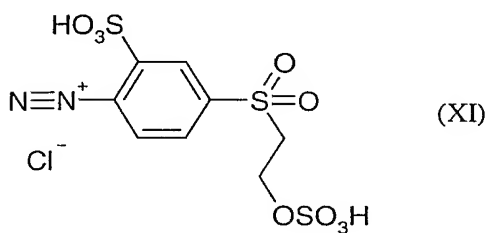
- 10 Example 1 is repeated except that the monoazo dye of the formula (VII) is replaced by 694 parts of the monoazo dye of the formula (IX)



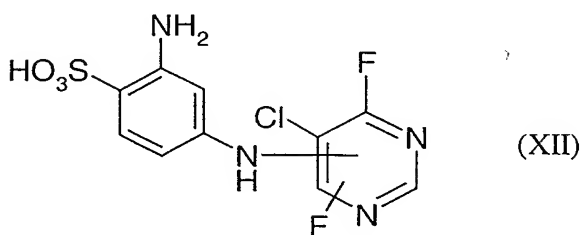
- 15 This affords about 2 600 parts of a greenish black salt-containing powder which dyes cellulose in deep bluish green shades. The dye conforms to the formula (X)



The monoazo dye of the formula (IX) is formed by coupling a suspension of the
 diazonium salt of the formula (XI) (prepared from 361 parts of 2-amino-5-(2'-sulphato-
 5 ethyl)sulphonylbenzenesulphonic acid)

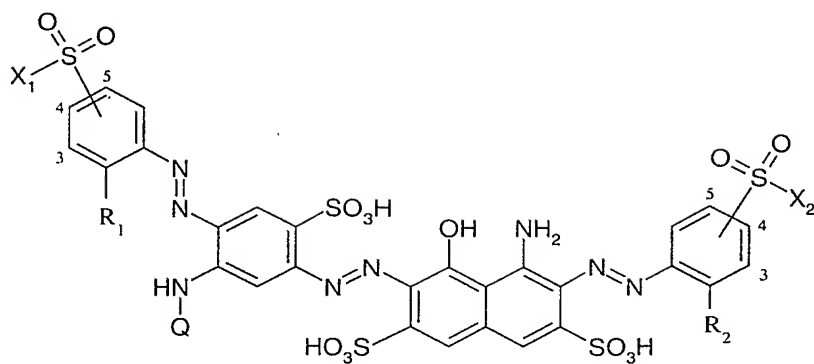


10 onto 367 parts of a condensation product of the formula (XII)



formed from 2,4-diaminobenzenesulphonic acid and 5-chloro-2,4,6-trifluoropyrimidine.

15 The remaining Examples 3-15 can be synthesized similarly to Examples 1 and 2.

**TABLE**

Ex.	X ₁	Position of SO ₂ X ₁	R ₁	Q	R ₂	X ₂	Position of SO ₂ X ₂
3	-CH ₂ CH ₂ OSO ₃ H	4	H		H	-CH ₂ CH ₂ OSO ₃ H	4
4	-CH=CH ₂	4	SO ₃ H		H	-CH ₂ CH ₂ OSO ₃ H	4
5	-CH ₂ CH ₂ OSO ₃ H	4	SO ₃ H	do.	H	-CH ₂ CH ₂ OSO ₃ H	3
6	-CH=CH ₂	4	SO ₃ H	do.	H	-CH ₂ CH ₂ OSO ₃ H	3
7	-CH ₂ CH ₂ OSO ₃ H	4	H		H	-CH ₂ CH ₂ OSO ₃ H	4
8	-CH ₂ CH ₂ OSO ₃ H	4	SO ₃ H		H	-CH ₂ CH ₂ OSO ₃ H	4
9	-CH=CH ₂	4	SO ₃ H		SO ₃ H	-CH ₂ CH ₂ OSO ₃ H	4
10	-CH ₂ CH ₂ OSO ₃ H	4	SO ₃ H	do.	SO ₃ H	-CH ₂ CH ₂ OSO ₃ H	4
11	-CH ₂ CH ₂ OSO ₃ H	5	SO ₃ H	do.	H	-CH ₂ CH ₂ OSO ₃ H	4
12	-CH ₂ CH ₂ OSO ₃ H	5	SO ₃ H	do.	H	-CH ₂ CH ₂ OSO ₃ H	3
13	-CH=CH ₂	5	SO ₃ H		H	-CH ₂ CH ₂ OSO ₃ H	4
14	-CH ₂ CH ₂ OSO ₃ H	4	H	do.	H	-CH ₂ CH ₂ OSO ₃ H	4
15	-CH ₂ CH ₂ OSO ₃ H	4	SO ₃ H	do.	H	-CH ₂ CH ₂ OSO ₃ H	4

USE PRESCRIPTION A

- A dyebath containing 0.3 part of the dye of Example 1 and 15 parts of Glauber salt (calcined) in 300 parts of demineralized water is entered with 10 parts of cotton fabric (bleached) at 60°C. After 30 minutes at 60°C, a total of 6 parts of sodium carbonate
- 5 (calcined) are added at intervals of 10 minutes in portions of 0.2, 0.6, 1.2 and lastly 4 parts while the temperature is maintained at 60°C. Dyeing is then continued at 60°C for one hour. The dyed material is subsequently rinsed in running cold water and then for 3 minutes in running hot water. The dyeing is washed off at the boil in 500 parts of demineralized water in the presence of 0.25 part of Marseilles soap for 15 minutes.
- 10 After rinsing in running water (3 minutes hot) the fabric is centrifuged and dried in a drying cabinet at about 70°C. This provides a green cotton dyeing having good fastnesses, which exhibits good light and wet fastnesses in particular and is stable to oxidative influences.

15 **USE PRESCRIPTION B**

- A dyebath containing 10 parts of Glauber salt (calcined) in 300 parts of demineralized water is entered with 10 parts of cotton material (bleached). The bath is heated to 60°C in the course of 10 minutes before 0.5 part of the dye of Example 1 is added. Following a further 30 minutes at 40°C, 3 parts of sodium carbonate (calcined) are added before
- 20 dyeing is continued at 60°C for a further 45 minutes. The dyed material is rinsed with running cold water and then with hot water and washed off at the boil similarly to prescription A. Rinsing and drying leaves a green cotton dyeing which has the properties recited for prescription A.
- 25 The dyes of Example 2-15 or dye mixtures of Examples 1-15 can likewise be used for dyeing similarly to prescriptions A and B. The dyeings obtained possess good fastness properties.

USE PRESCRIPTION C

A print paste composed of

	40	parts of the dye of Example 1
5	100	parts of urea
	350	parts of water
	500	parts of 4% sodium alginate thickening
	10	parts of sodium bicarbonate
	<hr/>	
10	1 000	parts in total

is applied to cotton material by the customary printing processes.

15 The printed material is steamed at 102 – 104°C for 4 – 8 minutes and then rinsed cold and hot. The fixed cotton material is subsequently washed off at the boil (similarly to prescription A) and dried. The bluish green print obtained exhibits good general fastnesses.

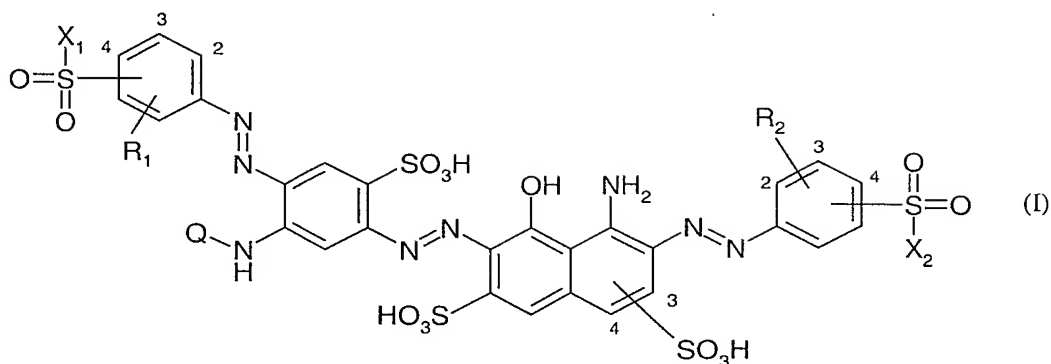
20 Examples 2-15 or dye mixtures of Examples 1-15 can likewise be used for printing cotton similarly to prescription C. Bluish green prints having good fastness properties are obtained in all cases.

USE PRESCRIPTION D

25 2.5 parts of the dye of Example 1 are dissolved in a mixture of 20 parts of diethylene glycol and 77.5 parts of water at 25°C with stirring. This solution can be used directly as a printing ink for printing by means of inkjet printing apparatus. The substances of Examples 2-15 or dye mixtures which contain materials of Examples 1-15 can likewise be used similarly to prescription D.

CLAIMS

1. Compounds of the formula (I)



where

X_1 and X_2 are independently $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}_2\text{Y}$, where Y is an alkali-detachable group,

R_1 and R_2 are independently H or $-\text{SO}_3\text{H}$, and

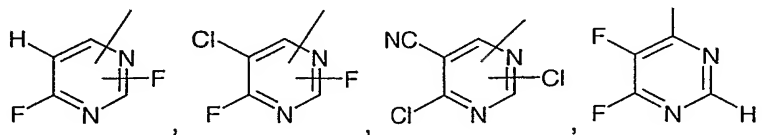
Q is a halogenated pyrimidine reactive radical,

and also their salts and mixtures thereof.

2. Compounds according to Claim 1, characterized in that

X_1 and X_2 are each $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{Y}$, where each Y is independently $-\text{OSO}_3\text{H}$, $-\text{Cl}$ or $-\text{SSO}_3\text{H}$, and

Q is one of the following halogenated pyrimidine reactive radicals:

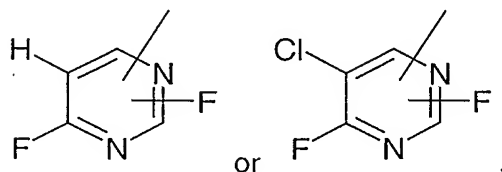


and also their salts and mixtures thereof.

3. Compounds according to Claim 1, characterized in that

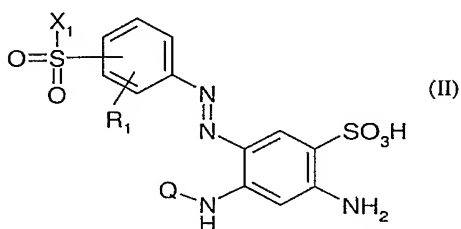
X_1 and X_2 are each $-\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$, and

Q represents the following pyrimidine reactive radicals:



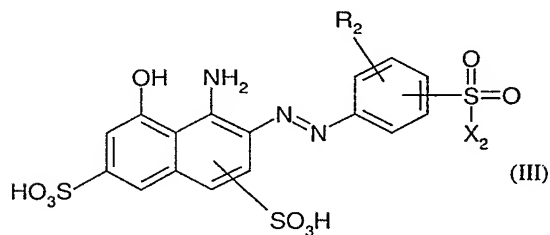
5 and also their salts and mixtures thereof.

4. Process for preparing compounds of the formula (I), characterized in that a compound of the formula (II)



10

where the individual substituents are each as defined in Claim 1, is diazotized and coupled with a compound of the formula (III)



15

where the individual substituents are each as defined in Claim 1.

5. Use of the compounds of the formula (I) and also mixtures thereof and their salts according to Claim 1 for dyeing or printing hydroxyl-containing or nitrogenous organic substrates.
6. Use of the compounds of the formula (I) and also mixtures thereof and their salts according to Claim 5 for dyeing or printing leather and fibre materials comprising

20

natural or synthetic polyamides or especially natural or regenerated cellulose, such as cotton, filament viscose or staple viscose.

- 5 7. Use of the compounds of the formula (I) and also mixtures thereof and their salts according to Claim 5 for dyeing or printing textile material comprising cotton.
8. Use of the compounds of the formula (I) and also mixtures thereof and their salts as a component in an inkjet printing ink.
- 10 9. Substrates, especially cellulose, polyamides and animal fibres, preferably cotton, dyed or printed with compounds of the formula (I) and also mixtures thereof and their salts according to Claim 1.
- 15 10. Substrates, especially paper and optionally pretreated substrates comprising cellulose, polyamides or animal fibres, printed with inkjet printing inks according to Claim 8.

INTERNATIONAL SEARCH REPORT

Interi nal Application No
PCT/IB 02/04100

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B62/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN & JP 63 199269 A (NIPPON KAYAKU CO LTD), 17 August 1988 (1988-08-17) abstract ----	1-10
A	JP 60 130562 A (BASF AG) 12 July 1985 (1985-07-12) the whole document ----	1-10
A	PATENT ABSTRACTS OF JAPAN & JP 2000 044830 A (SUMITOMO CHEM CO LTD), 9 December 1998 (1998-12-09) abstract ----	1-10
A	EP 0 065 479 A (BAYER AG) 24 November 1982 (1982-11-24) cited in the application the whole document ----- -/-	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

10 January 2003

Date of mailing of the international search report

22/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Baston, E

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/IB 02/04100

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 526 792 A (BAYER AG) 10 February 1993 (1993-02-10) cited in the application the whole document -----	1-10

INTERNATIONAL SEARCH REPORT

Intern	al Application No
PCT/IB 02/04100	

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 63199269	A	17-08-1988	JP 1987232 C JP 7013200 B	08-11-1995 15-02-1995
JP 60130562	A	12-07-1985	CA 1229345 A1 DE 3433977 A1 DE 3462134 D1 EP 0144800 A1 HU 36985 A2 ZA 8408937 A	17-11-1987 30-05-1985 26-02-1987 19-06-1985 28-11-1985 31-07-1985
JP 2000044830	A	15-02-2000	NONE	
EP 0065479	A	24-11-1982	DE 3118699 A1 BR 8202746 A EP 0065479 A2 JP 57195160 A	02-12-1982 19-04-1983 24-11-1982 30-11-1982
EP 0526792	A	10-02-1993	DE 4125754 A1 DE 59209083 D1 EP 0526792 A2 JP 5247365 A US 5538518 A US 5436324 A	04-02-1993 05-02-1998 10-02-1993 24-09-1993 23-07-1996 25-07-1995